



Paradigm shift in orthopedic implants from metals to polymers

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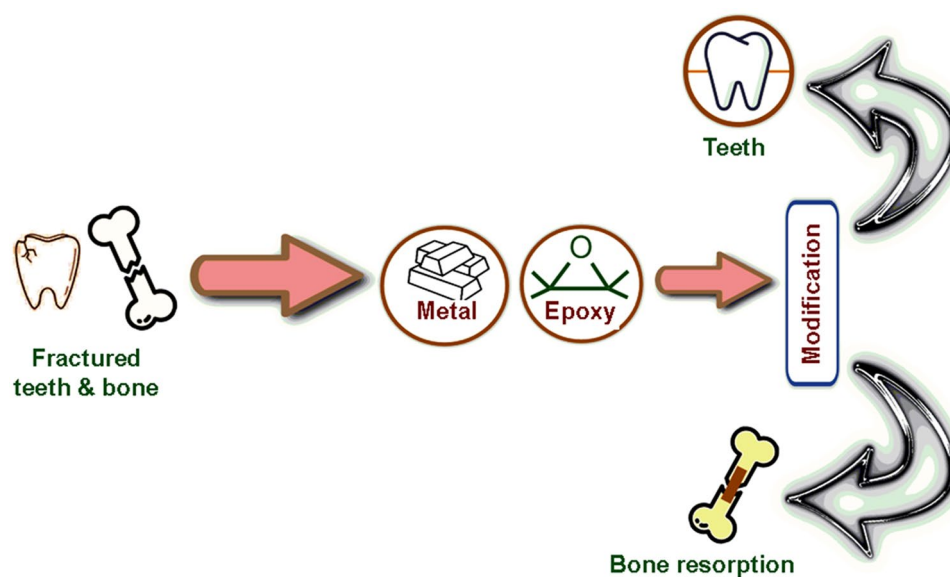
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Abstract

The creation of highly biocompatible advanced materials for use in orthopedics has long been a goal. Because of this need, orthopedic implants have progressed from metals to polymeric composites. Ancient orthopedic implants were mostly metals, but in the present age, advanced new materials in orthopedic surgery and prostheses have broadened the available options. Alternative forms of treatment are becoming increasingly possible with the upgrade of mechanical properties and improved quality of materials. The mechanical performance of advanced material is rationalized including tensile and flexural strength, elastic modulus, and wear resistance to assess their suitability for orthopedic applications. In recent eras, the novelty in research includes the use of reinforced polymer-based composite due to mechanical strength and stress shielding close to real human bone. Also, a comparative analysis of natural and synthetic reinforcement in composites proves that the former is biocompatible, eco-friendly, and economically cost-effective. The bioactivity of composites can be improved by surface modification with bio-coating to promote enhanced biomedical performance. This literature review contains data on different types of materials for prosthetic devices. It outlines mechanical and biological factors favoring material selection, particularly epoxy, for improved physiological functions of the human body, along with economic considerations influencing orthopedic surgery.

Graphical abstract



Keywords Epoxy · Orthopedic · Biomedical application · Bone replacement · Implants

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Introduction

In recent years, the field of orthopedic implants has witnessed a remarkable transition, marking a paradigm shift from traditional metal-based solutions to the innovative realm of polymers. This transformative shift not only underscores advancements in materials science but also holds the promise of revolutionizing the landscape of orthopedic treatments. As we delve into this intriguing evolution, we explore the driving factors, challenges, and potential benefits that accompany the adoption of polymers in orthopedic implant technology. Unlike previous reviews focusing on individualistic materials, this review provides a comprehensive and critical review of metals, polymers, and nanocomposites with their disadvantages of bioactivity and physiological conditions in the body and provides relative potential solutions with applicability in both bone and dental implants. Integrating material science and biomedical engineering accompanying advanced analytical techniques gives a clear understanding of their biocompatibility and mechanical properties for an interdisciplinary perspective to enhance the understanding of biomaterials to revolutionize implant technology. This review especially covers epoxy polymer-based composites synthesis by employing different methods to improve their mechanical performance and its clinical trials while considering applications in the diverse field [1].

Background of study

Advanced new materials have replaced ancient metallic orthopedic implants, with upgraded mechanical strength and quality [2, 3]. Fractures often occur in lower limb long bones due to high impact ratio or due to other extrinsic factors, including falls, sports injuries, vehicle accidents, military war, or intrinsic causes such as muscular action. United States Hospital Department of Emergency found in a study of pediatric amputation cases that the average age counted for traumatic amputations was approximately 6.2 years with annual prosthesis and medical care costs of \$206.8 million in 2015 [4]. Vascular disease and diabetes are leading causes of amputations in the US as 185,000 amputee surgeries are performed annually. The whole dental prosthetic market globally tends to be estimated to exceed \$5 billion [5]. Therefore, demand for bone substitutes globally is expected to expand progressively by 2030 reaching a market value of \$79.5 billion [6].

History

Prosthetic limbs came along about 3000 years ago. Back from 15th to nineteenth century was the era of custom-made

prostheses formulated by combining wood, leather, metals, and other materials. These limbs advanced in preceding times and could be flexed and controlled by springs, cables, and cranks, which enable them to bend and rotate. Metals have been used for more than one hundred years in bone implantation. Vanadium Steel was the 1st metal alloy to be used for implants [7, 8]. Metallic implants despite tensile strength, toughness, and time-reliant deformation, lack osseointegration and corrode in SBF (simulated body fluid) [9]. Titanium-based chambers were employed in the 1960s to check the path physiology of tissue injury and metals were found incompatible with take out during the healing process, which shows the unlikeness of metals with bones. Osseointegration leads to the failure of implants during clinical trials. Initially, trials were made to improve the condition of titanium alloys by coating them with hydroxyapatite (HA), but they were unable to resolve problems with biocompatibility and infection. In 1980, Bonefield et al. [10] came up with an alternative material, a polymer matrix, to substitute bone during implanting using polyethylene and HA. This leads researchers to use polymer composites in the biomedical domain for bone application [11].

Prosthesis

A prosthesis is an artificial limb. It could be a transradial prosthetic (missing arm below elbow) or a transhumeral prosthetic (missing arm above elbow). Leg prostheses may be transtibial prosthetic (below the knee) or trans-femoral (above the knee) [5].

Bone implant materials

Materials for biomedical applications are metals, polymers, ceramics, and composites, used individually or in combination to achieve desired properties. Ceramics and metals have 10 to 20 times greater elastic moduli than hard tissues. Polymer composites have high mechanical strength and stiffness as well as better adaptations with physiological conditions of host tissues, hence suitable for durable, fatigue/fracture resistant biomaterials [12].

Metals

Metals, owing to their exceptional mechanical properties, have been used for more than a hundred years. Alloys for orthopedic implants include iron, tantalum, titanium, tungsten, steel, and molybdenum. Metals have in vivo low corrosion resistance, which makes them incompatible with human tissue [9].

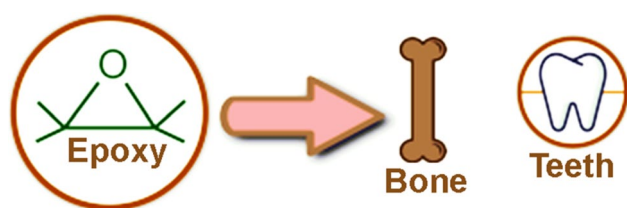


Fig. 1 EP resin applications

Table 1 Polymeric materials in orthopedics

Polymer	Application area
Silicone	Finger joints
PMMA	Bone cement
Polyester	Fixing breaks
Polyethylene	Knee amputation, artificial tendons, and ligaments, hip implants
PEEK	Finger joints, spinal implants, screws, and hip prosthesis

Polymers

Thermoplastic polymers are biocompatible due to moisture resistance, whereas thermosets such as epoxy (EP) are not, which limits their use in orthopedic applications (Fig. 1). Yet, they are preferred in fracture fixation as per their better processing characteristics. Hence, a properly processed and carefully chosen EP resin has biocompatibility and can be processed easily for structural applications in orthopedics [13]. Applications of some polymers in different orthopedic areas are given in (Table 1). Polymer implants are reliable, and their viscoelastic properties are comparable to natural bone [14]. Polymer material application in orthopedics is concerned with fixation elements or load-bearing joints. Mostly used polymer materials in orthopedics are ultra-high molecular weight polyethylene (UHMWPE), polyether ether ketone (PEEK), and polymethylmethacrylate (PMMA) [15].

Composites

Due to superior features, the concept of implanting composites into bone became popular in the 1980s [16]. Composites are used in several orthopedic fields:

In bone fracture: Polystyrene (PS) and PA-PTFE can be used as alternatives to Ti alloy due to low modulus and having high strength and enough stiffness.

In bone plates: It can be either made of thermosets, like carbon fiber (CF)/EP and glass fiber (GF)/EP, or

thermoplastics like CF/PMMA, CF/nylon, CF/PS, CF/PEEK, and CF/PE.

In bone cement: PMMA is primarily used and has been for more than 40 years. In intramedullary nails, they must be strong enough to support the body's weight due to their use in lengthy bone fractures, that is, GF/PEEK [17].

Ceramics

Ceramics consist of both metallic and non-metallic elements (SiO_2 , SiC , TiC , ZrO_2 , Al_2O_3 , etc.). Ceramic biomaterials in comparison to polymers and metals have fewer applications [18]. Bioceramics (bioactive glass (BAG) and calcium phosphate) have limitations due to low fracture resistance which decreases its use in vigorous strain and stress conditions [19, 20]. Bio-ceramic forms a mineral apatite-dense layer on the implant surface in vivo in the human body, which is similar to bone tissues and thus forms effective bonding with living tissues [21]. Calcium phosphate ceramics are important as their inorganic elements are similar to bone mineral components, which directs their use in bone tissue repair [22].

EP biocompatibility

Biocompatible materials for orthopedic applications along with biocompatibility must also have non-toxicity, corrosion resistance, durability, ductility, and lessen Young's modulus [8]. Metallic implants are the most researched material where higher stiffness compared to bones brings higher stress shielding, but an immense increase in stress shielding leads to bone mass reduction and adverse effects on the durability of the implant. Other major drawbacks are the high Young's modulus of metals compared to bones and corrosion fatigue behavior. To address these issues, new improved biocompatible materials have been formulated, including polymer composite with biocompatible coatings having high durability and load-bearing capacity [23, 24]. Polymer matrix composites have many structural applications in the industrial and biomedical domains due to compatibility with advanced medical technology of imaging as magnetic resonance imaging (MRI) and computer topography [25, 26].

Polymer matrix fabricated with compatible fillers would be a great area of interest for researchers [27–29]. Although researchers [30] found that a lot of EP resins have severe cytotoxicity and inflammatory response during implants, even then EP resins are used in different biomedical domains i.e., surgical tapes, canal root sealers, bio-adhesives, etc. This is due to incomplete curing or polymerization of EP monomers. Thus, non-toxic effect of EP through complete curing is needed for biomedical applications. An approach with a high curing percentage has been reported [31] as well

as filler surface chemistries have also been reported for augmented curing conversions [32, 33].

Epoxies have good thermal stability and mechanical properties which make them suitable for orthodontic applications, such as bone cement, dental restorations, and root canal sealers. The better aesthetic qualities of EP as compared to alloys and its similarity with the elastic coefficient of tooth make it a unique candidate for dental applications. EP resins have high brittleness which leads to their breakage during use. So, continuous efforts are exerted to obtain biocompatible, aesthetic, and better dental material by reinforcing the EP (Table 2). Reinforcing agents are used to obtain high mechanical properties to increase their strength and improve thermal stability without reducing toughness [34]. Epoxies still have a charm because of their hindered shrinkage, less than acrylics which ensures a possible reduction in internal stress and an optimal adhesive property even if they have less photo-reactivity compared to other conventional monomers such as acrylics [35]. CF/EP composites were used in dentistry for internal fixation due to non-cytotoxicity and great biocompatibility [36]. Diglycidyl ether bisphenol A (DGEBA)-based composites are preferred in dental applications. Sodium bioglass-based EP resins have been used for the past two decades in bone implants as per confirmed biocompatibility [37].

Epoxies implants

Bone is a structural anisotropic composite made up of collagen fibers and HAP nano-crystals (Fig. 2). Generally, bone fractures are treated in two ways i.e., external or internal fixation. The 1st one does not have any requirement for the opening of the fractured place while the latter needs the opening of the fractured place. Composite material is used in external fixation systems, such as casting, braces, and splints.

In external fixators, lightweight and stiff CF/EP composites are preferred, whereas for internal fixation bone plates and screws are used (Fig. 3). Rigid fixation complications involve bone atrophy beneath the metal plate. It may lead to bone refracture after plate removal as high-stress shielding leads to weak and less dense bone formation in the healing process. This suggests the use of less rigid fixations to reduce stress shielding, but on the other side, to bear high load material must have high stiffness and fatigue strength. Considering all these properties, polymer composites are promising candidates for either the partially resorbable, fully resorbable, or non-resorbable categories. EP-based thermosets due to toxic monomers are less significant in comparison to thermoplastics. In orthodontic treatments, materials mostly used are zirconia, silicate cement, acrylic resin, gold, and amalgam. Meanwhile, metals are used less due to inflammation and low aesthetic quality. Henceforth,

the choice of biomaterial depends on the quality, aesthetic, and mechanical properties of a material.

In dental implants, missing teeth are replaced with artificial teeth. Composites have high strength and low modulus, which makes them more suitable for dental implants than metal alloys and ceramics. Most people above the age of 50 have a full or partial layer of upper denture (false teeth). Metal-sensitive patients develop dermatitis and restrict their use of it. Ceramics although have good aesthetic quality but abrasive so only used for upper teeth brackets. Ramakrishna et al. [38] developed the functionally classified dental post using CF/EP polymer composite. Polymer composites with less abrasive wear and less friction characteristics are to be needed in orthodontics [39].

Reinforcement

Reinforcement's quantity and orientation equally are vital for adaptable mechanical and biological properties of implants, with host tissue. Orientation of reinforcement is required to create anisotropy in composites as human tissues are anisotropic [39, 40]. Nanoparticles (NPs) as reinforced in polymeric composites not only to increase mechanical and tensile strength but also to augment the anti-bacterial activity. Although their cost is a minus, it is covered by the fact that a small amount of NPs mends composite properties. Carbon nanofibers (CNFs) are used in orthopedic and dental implants due to their lightweight and mechanical strength. HA has also been used as a whisker as per its bioactivity and biocompatibility, even though it reduces the mechanical strength of composite [11]. Natural fibers (NFs) like banana, roselle, and sisal have also been used in bone implants [41]. NF-based composites are eco-friendly and biodegradable [42]. Fiber reinforcements, due to aspect ratio, enhance mechanical strength and modulus, but biodegradability brings mechanical weakness and non-recommendation for structural applications. Thermosets or thermoplastics composites with NFs have reduced the cost of the final product [43]. The use of particle shaped natural fillers aims to reduce polymer matrix for high filler content composites with enhanced mechanical properties, not to eliminate them from special applications [44]. Walnut (*Juglans regia* L.) powder, among all natural fillers, has the advantage of its ease of fabricating thermoset composites [45–47]. Particle reinforcement is economical, whereas fiber reinforcement is expensive and time-consuming. Stiffness and strength can be obtained by short fibers [48, 49].

Biomaterials in orthopedic implant

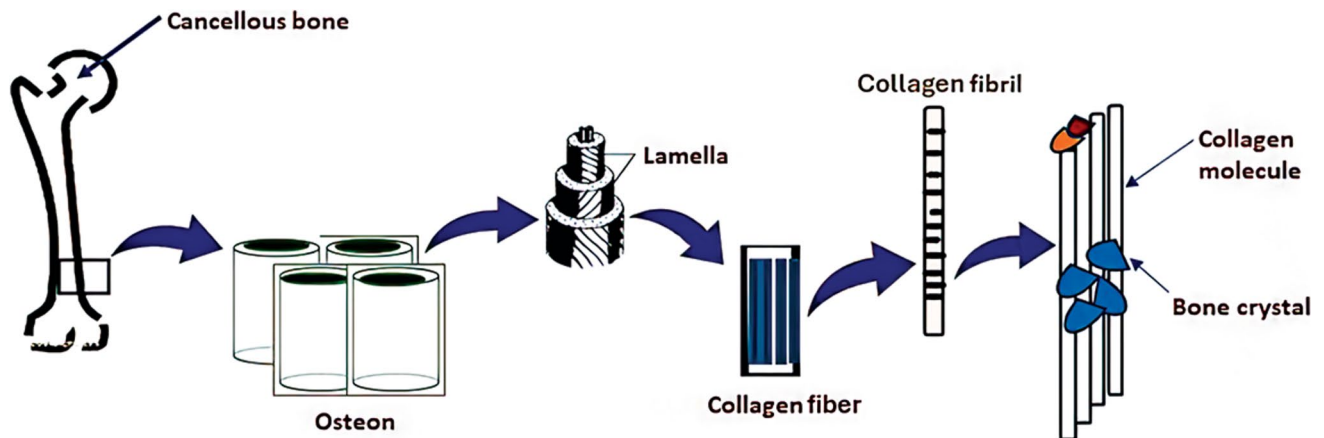
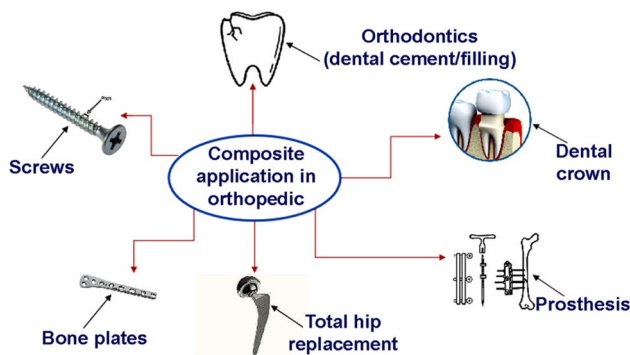
Biomaterials are engineered synthetic or natural materials for medical applications that are preferred to replace body parts that have become damaged due to disease, accident,

Table 2 Epoxy matrix, filler, and surface modification strategies in the biomedical domain

Matrix	Filler	Modification	System requirement	Application	Refs
EP resin	CF	NR	Curing technique	Internal fixation plates for limbs	[1]
EP resin	CF/Flax	Sandwich outside CF/EP inside Flax/EP	Compression molding	Application in bone fracture plate	[23]
2 layers of CF/EP sheets	16 layers of Flax/EP	NR	In compression molding machine	Long bone fracture fixation	[25]
Hyper-branched EP resin of BPA and glycerol (2:1)	OMMT and hydrophilic bentonite	H. aromatica oil for clay modification	Ultrasonication and curing	Tissue regeneration material	[30]
EPON 828 EP resin	Polyamide	NR	Cured 1 h/120 °C then 3 h/150 °C	In dental root canal posts	[34]
WSR618 EP resin	CF	Conc. H ₂ SO ₄ & CaCl ₂	Prepreg, curing, and demolding	orthopedic and dental implants	[36]
E-51 EP resin	Carbon nanofiber	Calcium phosphate to CNFs	Cure at 135 °C/1 h + 80 °C/12 h	Bone repairing	[40]
Cycloaliphatic EP	NR	Polyol	Curing by irradiating visible light	Dental material	[74]
EP resin	CF	NR	Curing at different temperatures	Ankle foot orthosis braces	[75]
EP resin	3D braided CF	NR	Vacuum impregnation technique	Osteosynthesis devices	[76]
EP resin (DGEBA)	SiO ₂	NR	Sol-gel technique	Application in bone cement	[77]
EP resin (ERL4221)	Silica nanoparticles	GPS as a modifying agent	Kerr Optilux (401)	Dental restorative material	[78]
SGFR EP	E-glass	NR	Injection molding and curing	Cortical analogue bone material	[79]
EP resin (CY219)	Non-woven cotton fiber	NR	Vacuum infusion technique	Orthopedic application	[80]
EP resin (LY556)	Hybrid Sisal, Hemp, jute fiber	NR	Hand layup process	Femur bone prosthesis	[82]
EP resin (LY556)	Sisal fiber	NR	Hand layup technique	Orthopedic implant	[83]
Hyper-branched EP based on bisphenol A	CNT-CuO-nystatin	Triton X-100 non-ionic surfactant	cured by reacting with poly (amido amine)	Biocompatible antimicrobial implantable material	[84]
Hyper-branched EP resin of Glycerol and BPA	silver-reduced graphene oxide- curcumin	NR	By Ultrasonication process	Anti-microbial in biomedical & marine field application	[85]
Rosin-based EP and COPU	MWCNT	NR	Hot pressing method	Medical treatment	[87]
EP, EP/ polyester	TiO ₂ nanoparticles	TiO ₂ as flow additives, CaO as bio-active agent	Cured at 200 °C in air flow oven	Dry powder coating application in implants	[88]
EP resin	MWCNT	Sandwich composites by Hand lay-up technique	By vacuum drying process & solution dispersion technique	Application of sockets in trans-femoral amputees	[89]
EP resin	Sisal, hemp, jute & banana	NR	Vacuum bag technique	Bio-composite for prosthesis	[90]
(DGEDP-ethyl) biobased EP resin	bacterial cellulose nanofiber	Trimethylsilyl to BC	Hot-press (80 °C/4 h) posture (160 °C/4 h)	High-quality Optoelectronic composite	[92]
EP resin	GF / Flax	NR	Compression molding technique	Orthopedic implant	[93]
R-EP (epo- 200)	HA/HA F	APTES modified HA	By blending and ultrasonication	Bone tissue replacement material	[94]
EP resin	GF/ Sisal fiber/ Chitosan	NR	Molding technique	Bone fracture plate application	[95]

Table 2 (continued)

Matrix	Filler	Modification	System requirement	Application	Refs
EP resin	TO nanoparticles	NR	Molding process	Biomedical application	[96]
EP resin (Super SAP 100/1000)	Bone ash	ball milling /Sonochemical	noncontact mixing process	Biomedical application	[97]

**Fig. 2** Nanostructure of bone**Fig. 3** Biomedical applications of EP composite

and aging [50]. Dated back to ancient civilizations, biomaterials have been used as artificial teeth, ears, bones, and joints as found in Egyptian mummies. Biomaterials must have the novelty to work in a pH range of 1–9, under stress (4 MPa) and load (3 times the body weight) along with biocompatibility and structural compatibility and to match surface and structural compatibility with host tissue.

Materials used in the biomedical domain are grouped into metals, polymers, ceramics, and composites which have their advantages and disadvantages depending on their applicability domain (Table 3). Chosen metals for implants include but are not limited to gold, stainless steel, nickel, tantalum, titanium, and metal alloys. In the polymeric section polyethylene, PMMA, polyurethane, and PEEK are

favorite ones. In bioactive ceramics, the most compatible are HAP, zirconia, titanium, alumina, and bioglass. Composites are widely used in orthopedic implants, but biocompatibility restrictions instigate researchers to explore materials with desired bioactivity towards internal use. The properties of biomaterials also depend upon the place where they are being used. For hard tissues like teeth and bone high tensile strength and elastic modulus are required so metals and ceramics may be applied (Table 4). Polymer-based nanocomposites such as PEEK reinforced with CNTs are used in spinal cages and dental implants. CNTs addition can improve mechanical properties as well as biocompatibility [51]. Metal-based nanocomposites such as titanium oxide alloys can be used in orthopedic and dental implants to harness coatings that have antimicrobial properties to resist implant infection [52]. Another example is the use of silver-incorporated stainless steel matrix composite without the need for surface treatment and other coatings as silver is susceptible to antimicrobial properties and implant infections [53]. Stress shielding is a drawback of metallic implants as it leads to bone porosity and mass reduction. Atrophy leads to the failure of the implant during the bone healing process. Polymeric composites have elastic modulus same as human bone which improves stress shielding [54]. Furthermore, these are suitable for implants due to their radiolucency and non-corrosive properties. Polymer fiber composites are appropriate for biomedical applications as per high strength and low elastic modulus [39] but are inadequate due to a lack

Table 3 Mechanical and biomedical properties of different biomaterials

Type of material	Mechanical properties and Young's modulus (GPa)	Application	Advantages	Disadvantages	Refs
Co-Cr alloys	High fatigue strength and wear resistance, 230 GPa	Joints and dental prosthetics	Corrosion resistance, exquisite mechanical properties, biocompatible and durability	Ion release and difficult to systematize, expensive	[119]
Titanium	High weight-to-strength ratio, 110 GPa	Dental and bone implants	Good biocompatibility and integration with bone, extended lifespan, corrosion resistance	Allergic reactions, Expensive	[121] [122]
Stainless steel	Elevated level of tensile strength, 190 GPa	Orthotic braces, Fracture fixation devices	Economically efficient, biocompatible, easy to shape, good mechanical strength, corrosion resistance	Low osteointegration and allergic, heavier compared to Ti	[123]
Mg alloys	Average modulus, lower density, 45 GPa	Bone screw and transitional implants	Similarity in mechanical strength to bone, biocompatibility, biodegradability	Complications by prompt biodegradation phenomenon	[124]
PGA	Tensile and compressive strength is 50–80 MPa and 100–150 MPa, 6–7 GPa	Tissue engineering for bone scaffolds, drug delivery, and biodegradable surgical sutures	High mechanical strength, non-cytotoxic, FDA-approved, highly biodegradable, excellent processability	Brittleness, hydrolytic rapid degradation	[125]
PLA	Average tensile strength, 2.7 GPa	Resorbable stitches and scaffolds in tissue engineering	Biodegradability, lightweight, biocompatibility	Inflammatory reaction, low in mechanical strength	[126]
PEEK	Same modulus as bone, 3.6 GPa	Dental and spine implant	Chemically inert, lightweight, radiolucent, biocompatible, fatigue resistance	Expensive, mechanical strength is lower in comparison with metals	[127]
PMMA	Tensile strength is 50–70 MPa, 2–3 GPa	In orthotics for restoration and fillings and bone cement	Easy to mold, excellent biocompatibility, physiologically stable	Cytotoxic as monomers release during polymerization, brittle, non-biodegradable	[128]
UHMWPE	Tensile and compressive strength is 40–50 MPa and 20–30 MPa, 0.8–1.5 GPa	Spinal and Maxillofacial implants, knee and hip joint replacement in orthopedic and cardiovascular components	Excellent chemical and wear resistance, high impact strength, and biocompatibility	Oxidative susceptibility, poor bonding to ceramics and metals, restrained processability	[129]
EP	Tensile and compressive strength is 50–90 MPa and 100–2000 MPa, 2.5–4.5 GPa	Bone implants and dental prosthesis	Biocompatibility, cytotoxicity minimal on proper curing, non-biodegradable, high mechanical strength and chemical resistance	Brittleness, a potential cytotoxic if not properly cured, unsuitable for resorption materials application	[130]
PCL	Tensile and compressive strength is 16–23 MPa and 16–40 MPa, 0.2–0.4 GPa	Tissue engineering, bio-adhesives, and drug delivery, in orthopedics implants for plates and screws	Highly biocompatible, non-cytotoxic, biodegradable, easy to mold and process	Lower mechanical strength for load-bearing application, slower degradation for resorption applicability, hydrophobic	[131]
HA	Lower in tensile strength, 80–120 GPa	Implant coating and bone grafting	Osteoconductive, aids in bone growth, good biocompatibility	Less mechanical strength, brittle, mostly used combining other materials	[132]
BAG	Lower in tensile strength, brittle, 35–100 GPa	Implant coating or filler material and bone grafting	Osteoconductive, good biocompatibility, aids in bone bonding	Less mechanical strength, brittle, mostly used combining other materials	[133]

Table 3 (continued)

Type of material	Mechanical properties and Young's modulus (GPa)	Application	Advantages	Disadvantages	Refs
Zirconia	High compressive strength and fracture toughness, 210 GPa	Head hip replacement and dental crowns	High strength, biocompatibility, corrosion resistance, excel in wear resistance and aesthetic	Phase transformation led to volume change, expensive	[134]

Table 4 Mechanical properties of hard tissues

Hard tissues	Tensile strength (MPa)	Modulus (GPa)
Cortical bone (longitudinal)	133	17.7
Cortical bone (transverse)	52	12.8
Cancellous bone	7.4	0.4
Dentine	39.3	11
Enamel	10	84.3

of osseointegration. Therefore, a compatible layer between bone and implant is needed for integration. Researchers have been trying to modify the surface of fabricated polymer composites.

Then positive and negative effects of different types of biomaterials depend on the required properties and special application of the implant. For example, metal-based nanocomposite is more fit for long bones and joint replacement as in load-bearing applications. Whereas for soft tissue implants, polymer-based composites show promising advantages. Ceramics-based composites are more suitable for bone fracture repair and dental implants [54]. Despite their benefits, implants have limitations, such as mechanical wear, tissue rejection, and corrosion [55]. Nanocomposites designed for biological properties must exhibit mechanical traits. For instance, adding antimicrobial properties assisted nanoparticles to a polymer matrix such as adding silver nanoparticles has been shown to lower the chance of infections due to implants [56]. It is also essential to take care of the possibility that nanoscale filler particles reinforced in a polymer matrix will move from the implant into the surrounding tissue and the bloodstream. The issue at hand can be remedied using biodegradable polymers as the matrix material and controlling the release of filler particles. These polymers can assist in lowering the risk of long-term toxicity by encouraging the implant's slow resorption and destruction over time [51]. Nanocomposite is a new field in medical implants that needs to address challenges, such as ensuring long-term biocompatibility and stability within the body, optimizing filler–matrix interface, and developing methods as some presented (Fig. 4), to evaluate the performance and safety of these materials. The implant performance can be enhanced in vivo by employing certain methods, such as surface modification, and nanocomposite coating for example BAG nanoparticles can be employed for surface modification of metallic implants to reduce the risk of implant loosening and favoring bone integration and growth [57]. Chemical functionalization of implants as chitosan gold particles functionalized by tyrosol can improve its adaptability to promote cell adhesion and combat fungal infection [58]. Nanopatterning of the implant surface can be done to improve cellular behavior, adhesion, and proliferation. For instance, the HAP

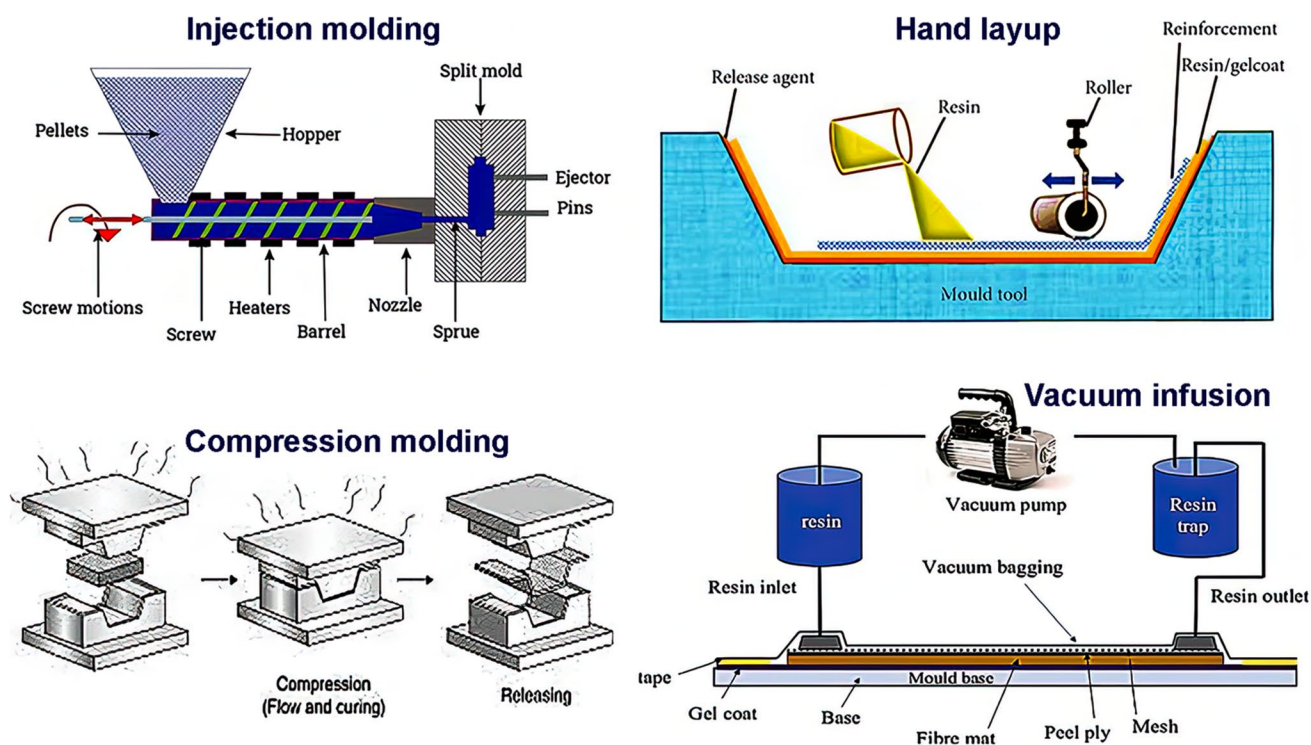


Fig. 4 Pictorial representation of different processing methods of biocomposite

or BAG-incorporated titanium implants with nano-patterned surfaces have shown improvised osteointegration in comparison to conventional implants [59]. By tailoring nanoparticles to different sizes and shapes with controlling techniques, such as precipitation, sol-gel, and hydrothermal techniques, for bone generation, imaging, and drug delivery applications [60]. Core-shell nanoparticles technique to improve implant performance like in magnetic resonance imaging (MRI), the magnetic core-shell nanoparticles can be used to enhance the contrast also giving a pace for targeted drug delivery and hyperthermia treatment [61]. Nanoparticles can be modulated by employing both doping and alloying techniques to increase nanoparticle properties like magnetism, electrical conductivity, and catalytic activity. One example is doping TiO_2 nanoparticles with nitrogen to enhance the cytotoxic properties of implants [62], while better material can be generated by alloying silver and copper nanoparticles with adaptable antimicrobial properties and electrical conductivity [63]. The properties of implant material can also be enhanced by employing corrosion resistance nanoparticles [64], self-healing [65], and multi-functional nanocomposites [66] which ultimately enhance corrosion resistance, durability, and biocompatibility whilst addressing other clinical needs. Choice of processing method for polymer-based biocomposites in dental and orthopedic applications depends on innumerable factors, comprising the type of matrix and filler used, desired properties of the final product, and the

specified application requirements. Each method used has its own number of advantages and disadvantages (Fig. 5) which needed to be carefully considered throughout the design and manufacturing process.

Bioactive coatings for orthopedic implant

Bioactive coatings help improve osteointegration and reduce osteoporosis through biocompatible bone and implant integration. HAP is the most demanding biocoating material due to its bioactivity, biocompatibility, and chemical similarity to bone mineral [9] but has limitations of stress shielding and refracture.

Researchers [11] have synthesized nano-fillers for biomaterials with compatibility to the human body. Duan et al. [67] have utilized selective sintering and other surface modification techniques to form poly (hydroxybutyrate-co-hydroxyvalerate)/3D calcium phosphate nanocomposites. The composites have shown regeneration of bone tissue cells. To enhance bioactivity and composite-bone interaction, CF/EP composite has been modified chemically for in situ bone mineralization. Functional groups like OH, PO_4H_2 , COOH, SO_3H have proven the nucleation of HAP. It has also been reported that Ca^{2+} release from the surface of the functional group causes the acceleration of bone apatite deposition [36].

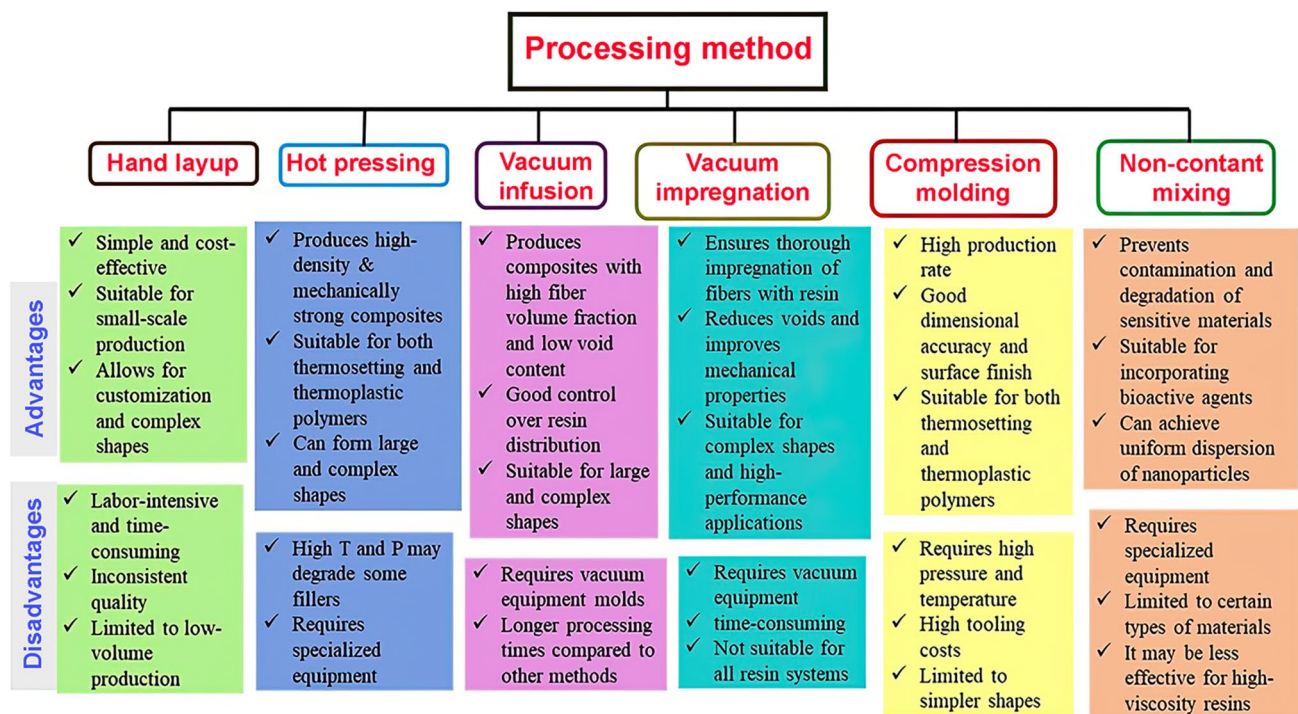


Fig. 5 Comparative analysis of processing method for polymer-based biocomposite materials

Currently, novel kinds of composites that can blend natural and synthetic biomaterials are desperately needed for the purpose of creating eco-friendly materials. The utilization of plant-based fiber-reinforced composites in biomedical applications is increasing because of their biocompatibility, promising economical production costs, and renewability [68]. By employing these composites in biomedical applications, we may offer an effective replacement for conventional materials like metals and ceramics, which may result in the development of medical equipment that is more ecologically friendly and sustainable [69].

The needs of the recent era emphasize the development of scientifically and technically improved biocompatible materials for biomedical applications. In the past few decades, prime importance has been given to the formation of highly compatible devices for bone replacement, tissue generation, and bone reconstruction in humans. The new era requires biocompatible material with high durability, flexibility, and enhanced mechanical properties with biological active properties for a long duration. So, increasing demand for biomedical improved material in orthopedics, such as bone implants, fracture fixation, bone filling, and tissue regeneration, acquires material with high material and bone surface bonding for a successful implication of materials in clinics. Bone implants, fracture fixation, and dental fillings first used metals and their alloys due to their ductility, toughness, and high mechanical strength but biological incompatibility, corrosion and wear resistance in in vivo body fluid issues limit

its application in the medical field. To overcome this issue, polymeric composites were employed [70]. In stress shielding, low modulus materials are required for bone implants, but low modulus polymers have low strength which restricts the use of polymers. Reinforcement is necessary to increase the stiffness, strength, and wear resistance such as CF/EP used in orthopedics because CF fabrication enhances the biomechanical properties of polymer resin. Epoxies have excellent thermal stability, mechanical properties, and corrosion resistance. In orthodontics, epoxies are employed for dental fillers and brackets due to biocompatibility with human tooth structure. However, high brittleness of epoxies due to enhanced cross-linking within the polymer network leads to its breakage during mechanism [71, 72]. The low stiffness and toughness of epoxy are much lower than metals. Therefore, efforts are made to develop composites by reinforcing EP resin with suitable fillers and enhancing its toughness and strength to make it applicable for orthopedic implants and dental applications.

Researchers [73] studied internal fracture fixation through CF/EP composite-based multi-axial plates, intending to avoid osteopenia (bone loosening), commonly observed after bone implant under metal plates. The CF/EP composites have great flexural strength and have 1/3rd the stiffness in comparison to the metal plates. These plates show greater results in upper and lower limb fracture fixation while tremendous results were obtained in sheep in vitro testing. To meet the need of new demands in orthodontics, this paper

[74] examines the simple polyol and epoxy ratio within the matrix and the selectivity of onium/camphor quinone as used cationic initiators for matrix cure to compare it with methacrylate. The selection of formulation constraints is the basic need to avoid cracking as the mass rise of the epoxy/polyol matrix was double in contrast to methacrylate polymer. The results show improvement in shrinkage as photocurable epoxy/polyol resin characterizes low shrinkage, high strength, and better glass transition temperature. Morrison et al. [75] proposed EP-CF composites to replace polypropylene resin in orthotic braces as per the disadvantages of heat production, overweight, and less load-bearing. EP-CF composites in partially cured form remain somewhat malleable, so adjusting the orthotic before curing is convenient. Flexural tests for both partially and fully cured composite showed strength no farther than 7%. This novelty leads to EP-CF composite use in orthotics where both stiffness and load-bearing capacity are required to facilitate patients with paralysis or musculoskeletal weakness in AFOs (ankle-foot orthotics).

Three-dimensional braided composite with exceptional fracture toughness and impact strength has a potential application in osteosynthesis devices [76]. C_{3D}/EP composite containing EP reinforced with 3D-CF when tested for load-bearing, volume fraction, and braiding angle has shown no brittleness due to increased void contents on load-bearing fracture. Augmented toughness made C_{3D}/EP composite suitable for fracture fixation due to enhanced braiding angle and high void content. Due to high void matter in C_{3D}/EP composite, Fickian model has no applicability. High moisture resorption as compared to pure EP has reduced mechanical properties but not at a significant level. Due to 3D braiding, C_{3D}/EP composite has application in strong load-bearing bone implants. Researchers [77] have prepared bone cement by covalent linking between EP and SiO₂. A precursor has been prepared by combining diglycidylether bisphenol A with 3-aminopropyl trimethoxysilane, which was co-condensated with tetraethyl orthosilicate. Comparative analysis of commercial bone with prepared bone cement presented the same tensile and bending strength but the prepared sample gave enhanced mechanical strength, low cytotoxicity, and less polymerization temperature for applicability as bone cement.

Methacrylate has been replaced with cationically cured cycloaliphatic EP with polyol [78]. Formulations were designed to avoid cracking in EP/polyol. Results showed improvement in shrinkage, high strength, and better glass transition temperature, along with problems of reaction heat and water uptake. Chen et al. [78] worked on low-shrinkage EP/silica composite as an orthodontics restorative material. EP (ERL4221) with 55% γ -glycidoxypropyl trimethoxysilane modified silica fibers were photo-cured. NPs showed good dispersion. Less shrinkage and coefficient of thermal

expansion (49.8 $\mu\text{m/m } ^\circ\text{C}$) have been observed in comparison to methacrylate (51.2 $\mu\text{m/m } ^\circ\text{C}$). High tensile strength (47 MPa) and micro-hardness (62 KHN) have been observed due to matrix–filler interfacial bonding.

Third- and fourth-generation bone analogs have been tested for biocompatibility and mechanical strength in orthopedic implants [79]. Third-generation cortical analog made up of EP short glass fiber has shown less fatigue and high crack formation compared to fourth-generation when used as a substitute for cortical bone. Fracture propagation and tensile properties of the fourth generation have been found close to natural human cortical bone. Data reported a 48% increase in fracture toughness of fourth-generation composites. Researchers [80] have also worked with non-woven cotton fiber for biomedical applications in orthopedics. 160% saline absorption was reported after cotton fiber reinforcement synthesized composites using the vacuum infusion technique. The creep recovery behavior of the composites was studied after saline absorption as specimens were immersed in saline at 37 $^\circ\text{C}$ for a variant time duration. Specific conditions for immersion were chosen which imitate the real conditions of humans. The saline uptake was double that of neat resin. The strain level of composites nevertheless increases above pure resin while creep strain decreases by 46.2% due to cotton fabric plasticization decreases prohibiting the mobility of the polymer chain in saline absorption. Results portrayed inter-facial de-bonding or higher deformation. Burger's model showed more ductility and reduction in elastic modulus along with an increase in plasticity, deformation, and viscosity. As confirmed by Burger's model fitting, results for composite samples were derived which makes it a potential candidate for orthopedic application. CF/Flax/EP hybrid composite has been reported [25] with high bending and less tensile strength than metals. This hybrid sandwich structure has effective mechanical properties with 2 layer prepreg sheets of CF/EP fixed to every outer surface of Flax/EP (16 layers prepreg sheets) core. Composites showed 510 MPa flexural and 399 MPa tensile strength, with fiber pull out and breakage at the fracture site which presented similarity to human cortical bones. The findings are worth considering for long bone fracture fixation. To address stress shielding and osteopenia, researchers [81] have made a comparison between metallic and CF/Flax/EP bone plates to treat Vancouver B1 fracture of femur injury. CF/Flax/EP composite showed bio-mechanical improvement with the same mechanical properties as bone. So, high toughness and low-stress shielding make the composite considerable for long-bone fracture fixation plate implant application. In another study, researchers [82] have prepared and characterized 12, 24, and 36% natural hybrid fibers (Hemp, jute, sisal) reinforced EP matrix (LY556) with hardener (HY 951). Compression, tensile, and bending tests were performed to check the structural compatibility of biomaterial for orthopedic

implants in a femur fracture. Results confirmed all prepared samples have strength as femur bone, but 36% composite showed greater mechanical strength, high density, and mass due to high fiber percent. Researchers have recommended the sample for internal as well as external orthopedic applications. Dinesh et al. [83] characterized wear resistance of EP (LY556), hardener (HY 951) reinforced with 10%, 20%, and 30% sisal NF for orthopedic implants. The result showed that 30% composite with improved wear resistance.

The fouling due to microorganisms is a worth noticing problem in biomedical fields. Barua et al. [84] prepared antimicrobial EP composites with 1%, 2%, and 3% (by weight) of MWCNT modified by triton X-100 surfactant and CuO and reported high tensile strength (38 to 63 MPa). Researchers [85] have also worked on antimicrobial thermoset hyperbranched EP composites reinforced by silver-reduced graphene oxide-curcumin. A green approach has been utilized to prepare nanohybrid material. 3% (by weight) composite inhibited *Staphylococcus aureus* and *Candida albican* growth. High elongation at break (17–21%) and tensile strength (54–65 MPa) have also been reported. Hyperbaric EP has also been reported in regenerative medicine and tissue engineering [30]. *Homalomena aromatica* rhizome oil-modified hydrophilic bentonite clay has been reported to be bio-compatible on the primary liver of Wistar rate RBCs, along with high thermal stability and better toughness. Composites inhibited *Staphylococcus aureus* growth and supported the proliferation of dermatocytes. Cross-linker (poly(amido amine)) imparted high mechanical strength. Antimicrobial behavior and mechanical properties make these nanocomposites a potential tissue scaffold material. An investigation of biochemical fatigue analysis has been conducted on CF/Flax/EP composites for application in bone fracture plates [86]. Conventional fatigue analysis and thermography analysis showed the same result for CF/Flax/EP fracture fatigue strength (200–220 MPa). The composites showed increased fatigue loading strength as compared to normal daily life in humans, retained up until the failure and minimized the activity of immunological response against the debris formation. Huo et al. [87] have worked on a bio-compatible, thermally, and mechanically stable composite from rosin-based EP with castor oil-based PU as a curing agent and CNTs as reinforcement. Hydroxyl functionalities on CNTs have covalently connected matrix and augmented T_g and thermal stability (initial decomposition from 284.5 to 305.2 °C for 0.4% (by weight) CNTs). Enhanced bio-compatibility has been observed through MTT cell viability assay for HeLa cells. In another study, 1,3,5-triglycidyl isocyanurate (TGIC) free powder coating was made using EP:Polyester (1:1 ratio) with 5% (by weight) CaO and nTiO₂ as bio-compatible stabilizers [88]. Particulate-sized coatings, made with sieves, have been sprayed on metal and cured at 200 °C. In in vitro, biomineralization study within 2–4 weeks of

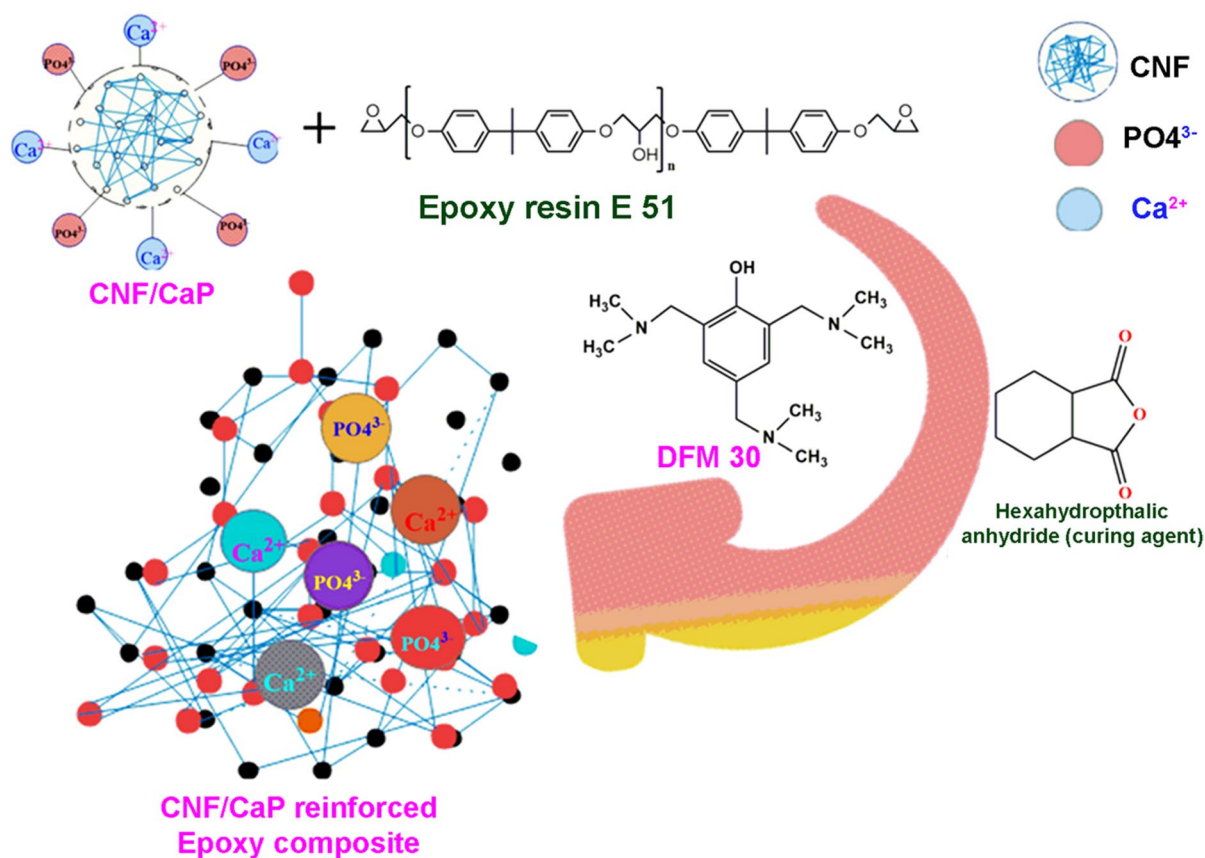
human mesenchymal cell culture development on the surface of composites showed that TiO₂ incorporated cellular response and polyester-TiO₂ enhanced biocompatibility of implant coating.

A major problem in the orthopedic application of bone repairing is the mismatch of flexural strength of prostheses with cortical bone. Gao et al. [40] worked on hybridized carbon nanofibers comprising calcium phosphate (CaP) as osteo-conductive fillers for EP resins. Results reported that the hybridized CNFs/CaP prepared by carbonization and electrospinning of polyacrylonitrile (PAN), and CaP gave a high-impact hybrid reinforcing phase in comparison to pure CNFs (Scheme 1).

EP-based sockets in leg amputation have issues like weight and heat accumulation, so multiwall carbon nanotubes (MWCNT) in 0.1–0.5% (by weight) have been introduced [89]. Composites showed enhanced thermal diffusivity and thermal conductivity, but mechanical strength decreased beyond 0.3% (by weight) of reinforcement. MWCNT (11.38% ± 1.5% (by weight)) improved flexural strength by 4–10 layers of stockinet. Compressive strength and modulus increment with MWCNT lead to a decrease in weight. Woven fabric of EP/E-glass with 0.3% (by weight) MWCNT increased heat transfer of amputees. This weight reduction and heat transfer of sockets is helpful in the transfemoral amputees to enhance the comfort level of these composites.

NF presents biocompatibility and cost-effectiveness in biomedical. Jagadish, et al. [90] studied the physio-mechanical properties of 16–24% NF (sisal, hemp, banana, and jute fibers) as a reinforcing agent in EP. 24% NF showed high tensile strength. An increase in fiber constituents in the matrix leads to the enhanced stiffness of the composite. NF-reinforced composites depict low density and high mechanical strength with increased solidity for biomedical and industrial applications. The limitation includes the weight gained so biocompatible coating was needed on naturally reinforced hybrid composite for weight reduction. Further analysis requires biocompatible coating and analysis tests to use composites for femur bone orthopedic implants.

Manteghi et al. [91] studied mechanical feasibility and the properties of a Glass/Flax/EP as a natural hybrid composite for potential application in bone fracture fixation. These Glass/Flax/EP composites are synthesized by the compression molding technique containing Glass/EP in the outer layer and Flax/EP as the core of the sandwich structure. This unique structure improves the hybrid composite more than prior applied clinical materials. Uniaxial tension, Rockwell hardness, and three-point bending test illustrate the high axial flexibility of composite material in comparison to metal plates. The water resorption test showed improvement by adding a glass layer to the pure Flax/EP composite. Stress shielding is useful for the fracture healing process. It shows



Scheme 1 CNF/CaP EP composite

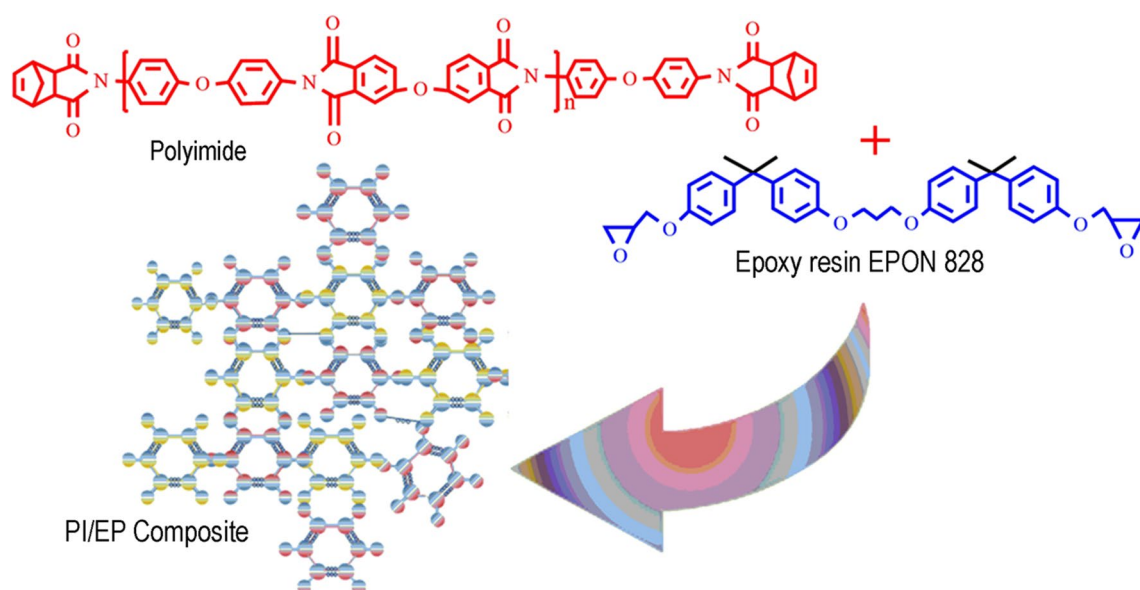
high stiffness and bending as compared to compression and tension. The primary failure as crack initiation, propagation, and secondary failure mechanism as delamination/de-bonding at the interface of two layers was noted as a limitation of composite material. These flexion qualities make composite material a potential application in bone fracture fixation due to its mechanical stability same as human cortical bone.

EP resins are biocompatible with elastic coefficient same as tooth structure but have intrinsic brittleness. Yang et al. [27] have reinforced EP with polyimide (PI) to impart strength, toughness, and aesthetics. Data reported that PI/EP composite has the strength of PI and toughness of EP (Scheme 2), which makes its use as a matrix of the fiber-reinforced material as root canal posts in dentistry.

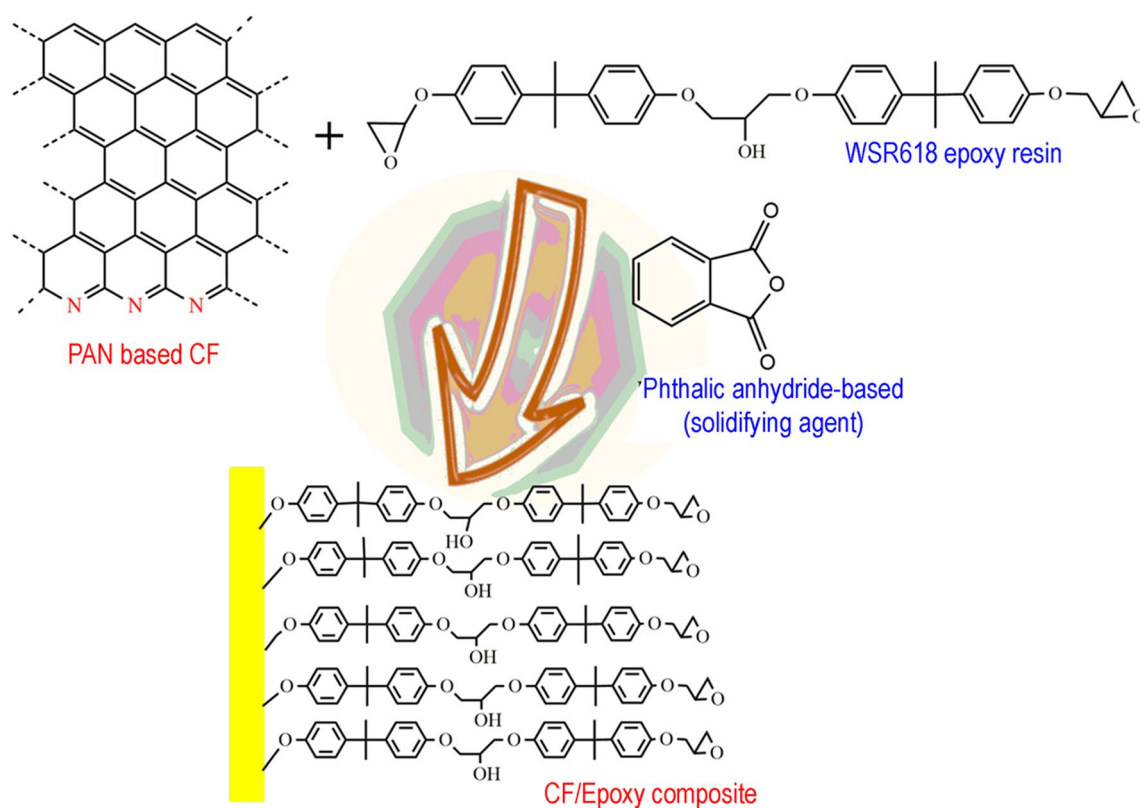
EP/CF composite during bone implantation showed a lack of direct bonding with autologous bone due to the inert surface of the composite. Surface chemical modification of EP/CF composite has been done by conc. H_2SO_4 (97% (by weight)) and calcium chloride to modify a composite surface for enhanced bioactivity and subsequently better bonding when in vitro simulated body fluid analysis of epitaxy formation is done. Cheng et al. [29] reported more Ca^{2+} ions deposition to form bone in SBF, while SO_3H ions caused the electrostatic force to form a dense and continuous apatite

strongly bonded with the substrate. Hence, a modified and economical CF/EP composite (Scheme 3) was obtained with applications in orthopedic, dental implants, and other medical fields.

Researchers [92] have also formulated bio-based high-performance nanocomposite reinforced with bacterial cellulose nanofiber by hot-pressing and curing method which leads to the advanced use of bacterial cellulose as a reinforcing phase for future research. Structural characterization of diglycidyl ether-based diphenolate ethyl ester (DGEDP-ethyl)/BCTMS, a bio-based EP composite was done as modified bacterial cellulose nanofiber network used with impregnation of trimethylsilyl moieties and adding bacterial cellulose (trimethylsilyl) fiber following the addition of resin mixture. As a result, diglycidyl ether diphenolate ethyl ester/ bacterial cellulose (trimethylsilyl) composite with 5%, 10%, 20%, and the 30% (by volume) bacterial cellulose TMS modified network loading respectively obtained with high Young's modulus and low density (Scheme 4). Manteghi et al. [93] worked on the compression and fatigue behavior of novel glass/Flax/EP-based composite, with both natural and synthetic fibers as reinforcing phases. The composites were synthesized as sandwich structures with two different configurations, named type A and B using unidirectional



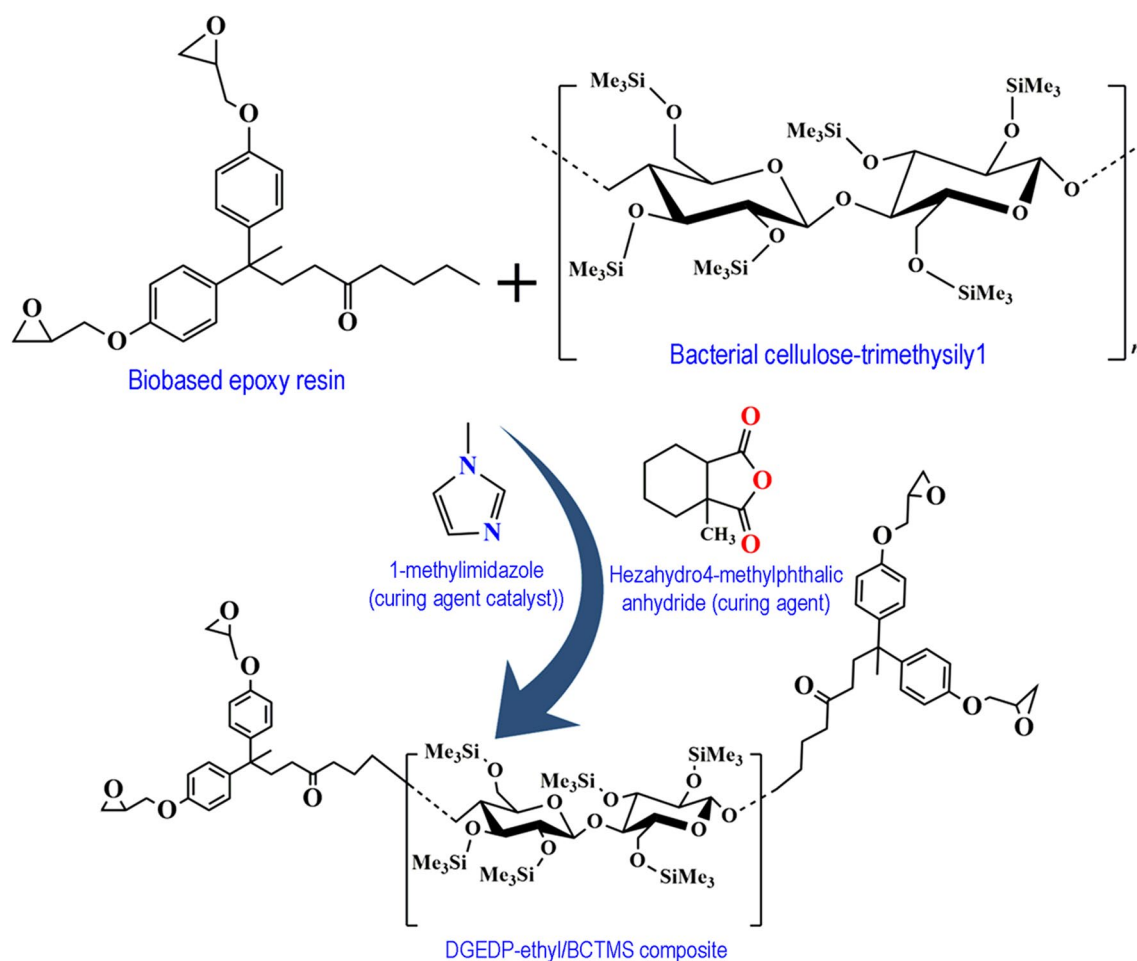
Scheme 2 PI/EP composite



Scheme 3 CF/EP composite

glass and flax fibers first, but later contained diagonal flax fibers. The composites were formulated by compression molding with a low void, depicting no debonding between the Flax/EP and Glass/EP interfaces. TGA employed in high

cycle fatigue strength measurement depicted 53% compressive strength for both A and B. High cycle fatigue strength for type A was 56–61% and for type B was 51–56% using standard fatigue strength experiment and compressive



Scheme 4 DGEDP-ethyl/BCTMS composites

moduli was 15 GPa for type A and 10 GPa for type B as dynamically constant during the entire loading mechanism. The limitation comprised primary and secondary failure mechanisms caused by crack initiation may be a reason that needs further micro-finite elemental analysis.

Composites based on non-modified HA and EP resin along with 3-aminopropyltriethoxysilane (APTES) were prepared and reported by Jaramillo et al. [94]. APTES was used for surface modification of HA, as amino groups enhance adhesion towards EP resin and other components and help in the functionalization of HA (HAF). Chemical methods, such as stirring and refluxing, at 25°C for 24 h were used for superficial modification. Composites were being prepared with 5% and 10% loading (w/w) by HA and HAF, respectively. Thermal and mechanical tests checked the impact of HA on crystallinity and thermal stability. The functionalization of HA enhances the thermal stability of the composite material and improves its dispersion in the resin matrix [94].

Hybrid SF/GF/CTS sandwich composite using EP as a polymer matrix has been utilized in orthopedic bone

plate preparation, with outer layers of GF/CTS/EP and an inner layer of SF/CTS/EP NPs, showing tensile strength of 146 MPa and bending strength of 343 MPa [95]. The SF/GF/CTS component has a hydrophobic nature while SF(sisal fiber)/CTS(chitosan) has a hydrophilic (contact angle $54.28^\circ \pm 3.06^\circ$). Obtained results make the sandwich composites of GF/SF/CTS-EP as a potential candidate for long bone fracture fixation.

The titanium oxide-EP nanocomposites were prepared using the casting method adding EP resin to titanium oxide (6%) in various contents of volume ratio. The result depicted that EP showed better tensile strength and mechanical properties when 1.5% titanium oxide was added. TO shows better Young's modulus as compared to single alone EP matrix and tensile strength of 14 MPa while the microstructure analysis shows TO as obstruction for crack propagation in composites. Thus, the results depicted due to high impact, tensile strength, and enhanced biocompatibility make the TO with resin matrix a better application in the biomedical domain [96].

Bone-ash reinforced bio-based EP upon 2% filler loading has shown a significant improvement in modulus (34.56%) and in flexural strength (41.25%) with better storage modulus and improved thermal stability which confirmed superior matrix–particle interaction. The improved thermal and mechanical properties of the EP composites allow them to have future potential applications in the biomedical field [97].

Metal incompatibility in long bone fracture plates led researchers to an alternative natural fiber, such as kenaf fabric and egg-shell powder-reinforced EP composite. The alkaline-treated kenaf fiber/EP composites were tested for mechanical properties with or without filler. The addition of 1–10% weight of eggshell filler showed 25–35 MPa enhancement in tensile strength. A maximum strength of 48 MPa was noted for carbonized eggshell filler, whereas un-carbonized (20% (by weight)) depicts tensile strength varying from 35 to 45 MPa. The result revealed 20% carbonized eggshell and 10% fly ash filler-based composite shows use as a femur bone plate instead of a conventional metallic fixator [98]. In another study [99], hybrid polymer composites for mechanical applications were prepared by reinforcing epoxy resin in 60% ratio with E-glass fiber and animal (ox) particulate in (20%, 30%, and 40%) ratio by hand lay-up method. The flexural strength is 250.43 MPa, tensile strength 254.96 MPa, and the compressive test shows maximum observed properties for 40% E-glass fiber ratio. Researchers [100] have also synthesized non-hazardous, renewable, and cost-efficient filler material in replacement of conventional material for prosthetic sockets. Seashell (SS) nanoparticles in 1%, 3%, and 5% (by weight) ratio and flax fiber (FF) 3 layers were reinforced in bio-based epoxy. The mechanical strength for finite and element levels shows increases in flexural and tensile strength with an increase in nano-particle mass ratio. 3% SS ratio shows an increase in tensile strength of 85 MPa and promising anti-bacterial properties for *Staphylococcus Aureus* and *E. coli* with respect to all SS/FF/EP composite. JF/SF/EP hybrid composite synthesized by vacuum bagging technique was examined for long bone fracture plates in orthopedic [101]. The mechanical test indicates 345 and 382 MPa as bending and compressive strength respectively. Young's modulus of 21.56 GPa was observed for the bending test, revealed higher than compressive 2047 MPa and tensile 6577 MPa modulus. The wettability test for composite scaffold showed the CA value of hydrophobic as 92.41 indicating JF/SF/EP composite as potent for orthopedics. Researchers [102] also developed and compared two different biocomposite materials for properties with the same stiffness as bone for bone defects. The EP matrix fabricated with 1%, 3%, 7%, and 15% weight ratio of seashell and HAP nanoparticles was synthesized and examined for mechanical strength. The 7% (by weight) ratio of SS nanoparticle in EP resin shows elastic modulus

as 37% and tensile strength as 46.7% in comparison to other weight percentage ratios of composite samples. FTIR shows no abnormality while DSC of samples shows little increase in T_g value with an increase in filler ratio. A biocomposite material for bone fracture fixation was synthesized as a hybrid composite of glass and carbon fiber reinforced in epoxy matrix by liquid resin infusion technique [103]. Tensile strength, elongation break, and modulus of elasticity were measured for composite samples. Low modulus and high mechanical strength of the sample as close to bone are promising aspects for low-stress shielding as compared to metallic implants for external fixation and bone implants.

HA nanobelts and carbon nanotubes in hybrid as (HN) were introduced onto the carbon fiber cloth by pulse electrochemical deposition and chemical deposition method combination as carbon fiber composites have promising use in the orthopedic field [104]. The HN was deposited on an anhydrous dicalcium phosphate-epoxy composite to optimize the mechanical and biological properties of the carbon fiber fabricated anhydrous CaP-based EP (CDE) composite. HN-modified CDE composite depicts strong mechanical strength as tensile strength and average friction increase by 52% and 45%, respectively. It also maximizes the elastic modulus by 170% compared to Unmodified CDE to model it as a promising candidate for orthopedic implants.

Due to the stress shielding defects, the femur bones which are often being treated with metal plates were in dire need of replacement with material that has similar stiffness to human bone. So, carbon flax fabricated bio-epoxy hybrid composites that were synthesized using the compression molding technique were introduced in recent research [105]. Tensile (9339.73 MPa), flexural, and wear test results show compatible results to human femur bone, and the possible near similarities make it a better replacement material as equal strength to femur bone causes less stress shielding. Further coating of composite surfaces could enhance the tri-biological properties. Bio-derived raw materials have proven to be a better choice to attain cost efficiency and mechanical strength. HA particles were synthesized from snails and eggshells in a 3–15% weight ratio and fabricated in epoxy resin to synthesize bio-based composites by stir casting technique [106]. Snail shell-based samples with a 15% weight ratio show higher mechanical strength as a modulus of 774.64 MPa and 40.25 as hardness index which is in comparison to HAP particles from eggshell. Hence, HAP particle reinforcement from snail shells with enhanced physical strength in the EP matrix makes it a stable candidate for biomedical application.

Multifunctional epoxy composites with excellent mechanical strength were prepared for post-dental fiber, orthopedic implant, and X-ray imaging technology [107]. The traditional fabrication method for reinforcing has prolonged production time and poor distribution. So, the multifunctional

filler (QF-Bi₂SiO₅) was prepared by radiopacity of quartz fiber and bismuth trioxide introduced to the EP matrix. Bending modulus and strength for the specimen are depicted due to the high interlocking of QF-Bi₂SiO₅ filler and EP. The QF-Bi₂SiO₅ was compared with other composite samples that had commercial fillers, but none showed both imaging functionality and mechanical strength for clinical application. An artificial composite material for bone application in surgery simulation was prepared by employing cellulose nanocrystals (CNCs) in 1%, 3%, and 5% ratio and bio-ceramics (HAP, zirconia oxide, and Yttrium-stabilized ZO) in 5% ratio with EP resin [108]. CNCs-added composites show an increase in ductility and stiffness with an increase in crystals ratio. The composite material of HAP as bio-ceramic and nano-cellulose, with 5% (by weight) and 1% weight ratio shows a compressive strength of 125.79 MPa, tensile strength of 32.13 MPa, and elastic modulus of 3495.19 MPa. This was similar in the mechanical properties numerically that of real bone [108].

The key aspect of the research was to synthesize a bio-based composite of EP resin with nano-silver (AgNps) and alumina particles at 1%, 2% and 3% (by weight) ratios to enhance mechanical strength and antimicrobial activity for dental applications. The Al₂O₃-AgNps/EP composite shows a positive effect for the 2% (by weight) ratio of hybrid nanoparticles. Due to poor adhesion and agglomeration of nanofiller in the EP matrix, there is a reduction in tensile strength and modulus while 1% (by weight) filler shows high impact strength and 2.5% (by weight) hybrid ratio of filler in EP-based composite shows high modulus and antibacterial activity for *S. Aureus* and *E. coli*. This study proves that a moderate Al₂O₃-AgNps ratio for dentistry is applicable [109]. In another study, an effort was made to recycle the ability of sandwich-shaped composite by fabricating flax and bio-based epoxy using liquid composite molding. Vacuum-assisted resin infusion and resin transfer molding techniques were used to assess the effect of production processes on mechanical ability depicting the former method for high flexural strength. 4 and 10 mm size recyclable for sandwich panel fabrication were used for size effect. 4 mm size sandwich panels of FF/EP composite exhibit better mechanical properties due to movement of inertia, and results for recyclable composite made it a requisite applicant for semi-structural application [110].

The pod sheath fiber-bamboo and green pea pod lignin hybridized EP composite was synthesized for prosthetic applications. The result shows 159 MPa tensile strength, 28.6 MPa as shear strength, and 202 MPa of flexural strength with 1% (by volume) of lignin inclusion. 82° of contact angle and 0.16% water absorption were indicated for 2% (by volume) lignin addition. A varying ratio of hybrid filler is used, and SEM results indicate that composite with surface treatment of fiber shows more uniform dispersion.

Researchers then analyzed 1% (by volume) of lignin with 40% (by volume) hybridized EP-based composite demonstrating the most favorable outcome for orthopedic application [111].

Bone implant materials were produced by the open mold method reinforcing calcium carbonate (CaCO₃) and reduced graphene oxide in epoxy resin matrix for bone tissue engineering application. The prepared sample was analyzed for its mechanical, physio-chemical, and biocompatibility. A tensile strength of 194.44 and flexural strength of 278.76 MPa were observed. The bioactivity test was done by immersing samples in SBF solution, and the result showed enhanced deposition of bone apatite crystals. It has improved antimicrobial characteristics against *S. aureus* (9.82 mm) and *E. coli* (8.75 mm). The MTT assay using the MG-63 (human osteoblast cell line) showed 78% viable cells for enhanced biocompatibility [112].

In this research [113], a tung oil-modified epoxy-terminated polyurethane (TETPU) was developed. The improvement in toughness along with exceptional mechanical strength owes to integrating sacrificial bonds formed by H bonds and π - π interactions within the EP resin network which is characteristic of biological material. The 30% inclusion of TETPU in comparison to neat DEGBA demonstrates a 40.29% enhancement in toughness, as well as impact strength of 90.59% and 111.7% elongation break. While flexural and tensile strength showed a decrease of 18.80% and 16.36%, respectively, with a substantial increase in toughness [113].

In another study, isophorone diamine (IPD) and diethylenetriamine (DETA) in different ratios were cured with neopentyl glycol diglycidate (NPG) epoxy [114]. T_g, biomineralization, and degradation behavior of DETA-cured EP resin demonstrate controlled T_g and biodegradability with basic and acidic conditions while tolerance to water. NGP-IPD composites containing HA demonstrate a prominent application for dental mineralization and bone repair applications. An apatite layer was formed on the NPG-IPD-HA composite by immersion in SBF. The apatite layer formation was due to lower T_g of NPGE-DETA which enhanced stickiness to make it suitable for adhesion and nucleation due to electrostatic absorption of ions by unreacted secondary amine moieties in SBF [114].

Researchers [115] synthesized CF/EP (DEGBA) composite by vacuum resin infusion method for biomedical applications. Then, with the intention of enhancing the mechanical strength of the CF/EP composite, surface oxidization of the CF was carried out in conc. HNO₃ at 100 °C to increase surface area and interfacial bonding of fiber and matrix. FTIR analysis indicated that oxidization of CF enhances the chemical functional groups, such as the -CO and -CN groups. A higher tensile strength of 45.60 MPa was observed for oxidized CF while 36.97 MPa for non-oxidized CF and

the result shows that higher tensile strength values were obtained when the longer the CF oxidation process took place.

Low velocity impact (LVI) test and the effect of various nanofillers on different types of composites with MWCNTs and alumina nanoparticles reinforced EP (828) resin were assessed. The enhancement in elastic modulus up to 163% and enhanced energy absorption capacity were demonstrated by the LVI test on the addition of types of nanoparticles simultaneously with the polymer matrix. The nanocomposites with reinforced fillers reduced the risk of sports-related injuries and improved safety and performance [116].

In this research, it was experimentally determined that UV-induced frontal polymerization allows curing time reduction to 1.5 min for EP resin tensile specimens in comparison to the traditional oven curing method for 15 h. The effect of weight content of PI, specimen geometry, and UV light intensity showed tensile properties improved for UV-induced frontal polymerization. It shows improved scale-up of FP technology for additive and sustainable manufacturing as well as repair of EP matrix and its fiber-reinforced composites as traditional curing limits in thermoset composites due to UV light being blocked by fiber components [117].

Another research [118] was done for large bone defects where artificial structural electrical bone scaffolds are needed. Barium titanate (BT) due to its stable charge surface and biocompatibility has applications in bone tissue engineering. BT has limitations in bone repair due to biological activity abate to promote mineralization and poor processability. EP acrylic-based composite combining 20% (by weight) CaSiO_3 with excellent piezoelectric properties for bone scaffold was prepared. By contrasting the light curing procedure with the conventional piezoelectric ceramic molding technique (dry pressing), the impact of the light curing process on the characteristics of the piezoelectric biological scaffold was examined. Even with the layered structure and pore characteristics attributed to 3D printing, the scaffold's mechanical and piezoelectric qualities are impaired. On the other hand, 3D-printed scaffolds could integrate piezoelectric and structural qualities, increasing their effectiveness against bacterial growth and deterioration. Piezoelectric features drive nutrients and proteins into the scaffold, which stimulates cell growth and differentiation in terms of cell activity [118].

Results and discussion

The advancement of the new era leads to the apex of technology in orthopedic and other biomedical domains. As the longer bones of limbs are more prone to fractures, implant materials diversified from metals to polymers, and its composites were used for internal and external fixators. Metals

have been used for centuries in implants owing to their durability and high tensile strength. Lack of mechanical wear, osteointegration of metal with host bone, and inflammatory response in vivo limits metal use [119]. Recent advancements in metals like surface coating and texturing improve bone-implant integration, reduction in bacterial adhesion and biocompatibility. Further developments for safe biodegradation were made for better outcomes in dynamic environments by processing smart super elastic and shape memory Mg and Zn alloys to cater the need of eliminating second removal surgery i.e., nitinol for orthotic stents and wires. However, despite these advancements, metals remain prone to complications in the physiological environment. Polymers later replaced conventional metallic implants, as they have high tensile strength, stress shielding, and elastic modulus as real bone. Polyethylene is corrosion and abrasion-resistant, so it is a viable polymer material for its bio-inert properties [120]. Polymer-based composites have advantages over other materials in all aspects, but their bio-compatibility and short-term stability limit them and pose a challenge to their performance. Metals and polymers are sometimes hybrid with ceramics as composites are used to create biomaterials with superior properties. The catastrophic failure in stress is due to the inherently brittle nature of ceramics and limited resorption due to slow degradability making them not an ideal potential for all applications. Researchers are trying to form biomaterial with durability, high mechanical strength, and anti-inflammatory with the physiological conditions of humans. The latest clinical trials were made to form bio-inert materials in SBF that have bioactivity and self-healing abilities for medical applications. The primary challenge that poses a barrier to the production of nanocomposite is high-cost production due to the complexity of the manufacturing process and the threat to achieving desired properties due to the non-uniform dispersion of nanofiller in the matrix. Several methods are employed to achieve this goal of uniform dispersion including mechanical mixing, solution-based method, in situ polymerization, surface modification of nanoparticles, electrostatic stabilization and magnetic stirring methods, and other advanced manufacturing techniques. Mechanical mixing constitutes high-energy ball milling. It gives uniform dispersion as a homogenous mixture and has limitations as introduced contamination and defects. Another is ultrasonication which agglomerates particles and is widely used for effectiveness and simplicity. The solution-based method involves sol-gel (for ceramics nanocomposites) and electrospinning (for nanofibrous scaffolds for tissue engineering). The in situ method involving CVD and the emulsion polymerization both give a high degree of dispersion while modification involves functionalization by grafting and surfactant use. The advancement in methodology involves 3D printing, which allows precise concentration and placement control of fillers in a matrix.

Another widely used method is melt compounding which uses a molten polymer matrix for polymer-based composites. Innovations in bio- and nanostructured ceramics, multi-functional nanocomposites, smart and biodegradable metals, and responsive and hybrid polymers will shape the future of orthodontics and orthopedic implants. Advanced manufacturing processes like electrospinning and 3D printing will make it possible to create customized, patient-specific implants with improved functionality. Enhanced mechanical qualities, biocompatibility, and patient outcomes are all envisioned with such advances.

Mechanical and biomedical properties of different biomaterials

Metal alloys, due to their remarkable mechanical properties, including high strength, wear and fatigue resistance, and durability, are ideally suited for a range of biomedical applications, including cardiovascular devices, dental prostheses, and joint replacements. Their outstanding biocompatibility and corrosion resistance ensure long-term stability within the body. Co–Cr alloys are expensive and difficult to machine, and some types contain nickel, which may cause allergic reactions in sensitive individuals. Additionally, emission of Co and Cr ions over time sometimes poses health risks. In spite of these challenges, their outstanding performance underpins their widespread application in rigorous medical implant scenario [119]. Ti alloys are commonly used in biomedical applications due to their remarkable strength, resistance to fatigue, corrosion resistance, high strength-to-weight ratio, and excellent biocompatibility. While commercially pure Ti alloys exhibit exceptional corrosion resistance, their comparatively lower strength renders them less ideal for load-bearing applications. Ti alloys offer certain advantages; however, they are also expensive, difficult to process, and some variants may release harmful metal ions that can trigger allergic reactions. Alloys that include molybdenum or niobium, like Ti-6Al-7Nb and Ti-15Mo, provide enhanced biocompatibility and a reduced modulus to decrease the stress ratio [121, 122].

Stainless steel, in particular, offers excellent corrosion resistance, remarkable mechanical properties, and is cost-effective, which makes it a favored option for biomedical applications. Cardiovascular devices, surgical equipment, and implants often feature their presence. Nonetheless, their application is limited in high-wear, long-term scenarios because of concerns regarding Cr and Ni ion leakage and diminished wear resistance. Variants featuring higher purity, like the 316LVM composition, offer enhanced fatigue resistance and biocompatibility. Stainless steel remains a practical and versatile material for a range of medical applications. [123]. Mg alloys are gaining popularity in biomedical

applications because of their biodegradability, lightweight nature, and biocompatibility. These attributes render them ideal for temporary implants like screws, stents, and bone plates. Mg alloys such as WE43 exhibit high strength and a slower rate of deterioration, while Mg–Ca is beneficial for bone repair but degrades too quickly, producing hydrogen gas in the process. These alloys reduce the necessity for repeated procedures; however, they present significant challenges due to their swift corrosion, inadequate mechanical strength, and leakage of hydrogen gas. Despite these challenges, Mg alloys remain a viable choice for short-term, load-bearing implants [124].

The orthopedic implant market is going through a major paradigm shift as sophisticated polymers replace conventional metal-based technologies. This transition is propelled by the increasing need for implants that provide superior biocompatibility, less toxicity, and increased osseointegration. Implants composed of polymers, such UHMWPE and PEEK, demonstrate enhanced mechanical characteristics, corrosion resistance, and diminished stress shielding. Moreover, polymers facilitate the creation of bespoke, 3D-printed implants tailored to the specific requirements of particular patients.

Polyglycolic acid (PGA) is a versatile and widely used biodegradable polymer in biomedical applications, particularly in tissue engineering and sutures. Its exceptional biodegradability, robust tensile strength, and biocompatibility make it suitable for short-term applications. Its brittleness, rapid deterioration, and unpredictable mechanical properties, however, must be addressed if its effectiveness in therapeutic settings is to be maximized. All things considered, PGA is still a promising material for a range of biomedical applications, especially those that need tissue integration and slow absorption [125]. Polylactic acid (PLA) is a versatile biodegradable polymer commonly employed in sutures and tissue scaffolds. It decomposes into non-toxic lactic acid over a period of six months to two years. PLA exhibits excellent moisture retention and thermal stability; yet, its brittle nature may lead to easy fracturing and diminished impact resistance. Disintegration rates can vary, and some people may experience localized inflammation that affects the scaffold's effectiveness. Although its quality may vary based on the manufacturing process, PLA is an affordable material [126].

When it comes to material suitable for permanent devices, PEEK maintains its structural integrity over time and can withstand sterilization processes. It possesses exceptional mechanical properties, biocompatibility, and thermal stability, and is a high-performance, non-biodegradable polymer commonly employed in biomedical applications, including spinal implants and prosthetics. Its accessibility may be limited, however, due to its higher cost relative to alternative materials and the potential for foreign body reactions.

Ultimately, PEEK is a suitable choice for fundamental medical applications requiring performance and endurance [127]. Because of its excellent mechanical strength and clarity, PMMA is a versatile, non-biodegradable polymer that is frequently employed in biomedical applications including intraocular lenses and bone cement. It provides stability and biocompatibility over time, but in some situations, it can be brittle and cause inflammatory reactions. PMMA is affordable, which makes a range of medical equipment possible. However, its use is limited to certain applications because of its low chemical resistance and deformation at high temperatures [128].

Because of its superior wear resistance, biocompatibility, and stability, UHMWPE is a very effective polymer that is widely employed in biomedical applications, especially in joint replacements and orthopedic devices. Long-term performance is guaranteed by its non-biodegradable nature, but problems like decreased tensile strength and possible wear debris-induced inflammation need to be resolved. All things considered, UHMWPE is still a useful material for a variety of medical applications, particularly those where performance and durability are essential [129]. EP resin has excellent mechanical properties, such as high tensile strength, good adhesion, and resistance to degradation and, is widely used in biomedical applications. However, despite these advantages, EP can exhibit brittleness and a tendency to absorb moisture, which may compromise performance in some applications; additionally, the presence of unreacted amines in some formulations can lead to cytotoxicity, necessitating careful formulation and processing. EP are versatile thermosetting polymers that are widely used in biomedical applications. Ongoing research is necessary to optimize their properties for particular biomedical applications while addressing biocompatibility and mechanical limitations [130].

Polycaprolactone (PCL) with exceptional mechanical flexibility, biodegradability, extended degradation time, low melting point, and long degradation time makes it a principal polymer for drug delivery and tissue engineering. However, low tensile strength confines its use in load-bearing applications and necessitates other reinforcement materials [131]. HA is a bioactive ceramic with excellent osteoconductivity that mimics the mineral component of bone and has good biocompatibility to make it suitable for coatings and bone grafts in implants. Poor mechanical strength and brittleness limit its use in load-bearing applications [132]. The BAG increases the bone regeneration process by forming an HA apatite layer when in contact with SBF, supporting cell differentiation and attachment. The major drawback of BAG is its brittle nature, which limits its mechanical applications [133]. Zirconia, a tough and strong ceramic which have good biocompatibility and wear resistance, has common use in orthopedic and dental prostheses. Zirconia with surface

degradation can undergo phase transformation in specific conditions [134].

Conclusion

In conclusion, the journey from metals to polymers in orthopedic implants signifies a pivotal chapter in medical innovation. The transition has not only demonstrated the adaptability of materials science but has also paved the way for enhanced biocompatibility, reduced implant-related complications, and improved patient outcomes. Advanced scientific approaches have facilitated human beings by providing a range of materials to replace damaged and deteriorated orthopedic components. Each material has specific pros and cons, but EP has been a prominent candidate in this race due to its mechanical strength and bio-compatibility. While challenges persist, the ongoing research and development in polymer-based orthopedic solutions present a promising avenue for continued advancements. The biomedical field has gone through a revolution due to the capacity to personalize and tailor composites, including the manufacture of implants tailored to each patient using modern manufacturing processes like 3D printing. Moreover, employing multifunctional composites has antibacterial qualities to prevent infections and provide therapeutic chemicals like growth hormones or antibiotics in response to specific biological signals i.e., Mg nanoparticles-based nanocomposite. Even with these developments, problems like maintaining long-term stability and intricate production procedures still exist. To create intricate and patient-specific implants, potential future aspects include the development of smart composites with responsive characteristics, improved biocompatibility, and sophisticated production procedures. With consideration, composites are a huge advancement in bone and dental implantology, providing better patient outcomes, safety, and function. As we embrace this paradigm shift, the potential for more effective, durable, and patient-friendly orthopedic implants becomes increasingly evident, shaping a future where polymers play a central role in the evolution of medical technologies.

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